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FUEL CELLS: A STATE-OF-THE-ART SURVEY

Report No 82-444-K

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ABSTRACT

The status of development, possible applications limitations and further development needs of different fuel cell types have been reviewed. in order to identify research areas where Ontario Hydro can make contributions to this developing technology and gain in-depth knowledge of associated material and technological problems. Phosphoric acid fuel cells are at the most advanced stages of development but further cost reduction and life prolongment are necessary in order to improve their cost competitiveness with other methods of power generation. Alkaline fuel cells appear ideal for automobile propulsion. Lowering of precious metal catalyst requirements and availability of low cost electrolytic hydrogen are necessary before they can penetrate the market.

job	file	date	report no.
740631-553-082	836.75	December 31, 1982	82-444-K

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EXECUTIVE SUMMARY

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Fuel cell power packs offer high energy conversion efficiency, low noise and exhaust emissions, low maintenance, modular design and short installation lead times. In Hydro, applications for these fuel cells can be found in centralized and decentralized generation, peak shaving, front end electrolysis-tritium removal plants and auxiliary power systems for emergency lighting. The objective of this state-of-the-art review is to evaluate the different fuel cell technologies that can be used in one or more of the above applications and identify research areas for Hydro's electrochemistry research program.

Alkaline fuel cells have been developed to a sophisticated level for space applications. They operate at moderate temperatures (60-80°C), offering high performance and short start time. Although most commercial alkaline fuel cells use precious metal catalysts, cells with non-noble metal catalysts such as Ni, are being developed at bench scale. The main limitation of these fuel cells is the requirement for CO_2-free hydrogen fuel and oxidant. Therefore, the use of the alkaline fuel cell is limited to specialized applications where pure hydrogen is available and affordable.

Phosphoric acid fuel cells are technologically the most advanced. They operate at 120-215°C and can be adapted to run on a variety of reformed hydrocarbon fuels. CO in the fuel gas acts as an anode poison and must be removed by oxidation or methanation. An increase in the operating temperature improves the CO tolerance of the cells but at high temperatures the problem of catalyst sintering becomes predominant. Improvements in sintering resistance and CO tolerance are possible with the development of new electrolytes and electrocatalysts.

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Solid polymer electrolyte (SPE) fuel cell technology is highly developed and is based on a hydrated Nafion (a sulphonated analogue of Teflon) membrane that serves as the separator, electrolyte, and support for precious metal electrocatalysts. SPE fuel cells yield energy efficiencies of 54% at an operating temperature of 65°C and a current density of 800 mA/cm^2. Due to the high cost of Nafion and the precious metal catalyst, their use is limited to special applications. SPE power plants of up to 5 kW have been tested. A detailed study of parameters critical for scale up is necessary in order to produce larger systems.

Molten carbonate fuel cells operate at high efficiency with low material costs. Operating at temperatures of 500-750°C, they are well suited for cogeneration and are capable of oxidizing hydrocarbons without any external reformation. However, the long-term performance of these cells remains to be demonstrated. Further development work is needed to stabilize the electrolyte, improve sintering resistance and the stability of electrodes.

Like molten carbonate fuel cells, solid oxide electrolyte fuel cells operate at high temperatures, ie 1000°C, and the electrode reactions are practically free of activation polarization. The cells are tolerant to CO and internal fuel processing is possible. Solid oxide fuel cells are being developed at laboratory scale and are not projected to reach pilot stage in the near future. Technological problems related to interconnection materials, cracking of cells and instability of solid oxide electrolyte appear to be immense.

The applications of fuel cells depend upon their electrochemistry, engineering and relative economics of operation. Since different applications can tolerate different levels of cost and performance, each type of fuel cell may not be ideal for every application.

Phosphoric acid fuel cell technology is best suited for centralized generation (>100 MW). Later, the molten carbonate and solid oxide fuel cells can replace or supplement the phosphoric acid cells as generation II and III technologies. Phosphoric acid cell technology is also well suited for decentralized residential and commercial generation (25-500 kW), where low temperature waste heat can be utilized for space and water heating. In the future, molten carbonate fuel cells will find major application in decentralized industrial generation (1-20 MW), where high temperature steam is required.

Current fuel cell and water electrolyser technologies are not suitable for peak shaving applications. The overall efficiency of an energy storage system based upon hydrogen storage is very low compared to other methods of power storage.

Alkaline fuel cell technology is well suited for transportation applications. However, the chances of having suitable hydrogen storage systems appear uncertain, at least in the near future. Direct methanol - air cells offer a great advantage of easy methanol handling and distribution. Unfortunately, little effort is being made to develop these fuel cells.

Alkaline and SPE fuel cell power plants could be used to supplement existing auxiliary power sources such as the ones for emergency lighting.

SPE fuel cells can be used to recombine detritiated D_2 stream with O_2, in a front end electrolysis-tritium removal system.

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To Mr. F.J. Kee
Director of Research

FUEL CELLS: A STATE-OF-THE-ART SURVEY

1. INTRODUCTION

As an electrochemical device, the fuel cell avoids the Carnot cycle efficiency limitation of thermal machines, thus offering the potential of high energy conversion efficiency. Fuel cells could serve the utility power system in several ways:

a) relatively small fuel-cell power plants (25-500 kW) using natural gas could be set up in residential and commercial buildings,

b) large plants (5-25 MW) could be dispersed throughout the utility network system to perform load following duty effectively, and

c) fuel cells could be integrated with coal gasifiers to provide large central base load power plants in the future.

Unique advantages of fuel cell power plants include:

- High energy conversion efficiency.
- Very low noise and exhaust emission levels.
- Vibration free operation.
- Little or no cooling requirement.
- Very little maintenance.
- A modular design which results in very short lead times for installation.

Because of these unique advantages offered to the electric power system by fuel cells their development has been continuously monitored and evaluated by Ontario Hydro for some years/1,2/. A more detailed assessment of fuel cell power plants for power generation has been made by the Design and Development and Research Divisions/3/. This study concluded that the high cost of present fuel cells and requirements for exotic fuels (H_2, steam reformed methane) make fuel cells uneconomic in relation to other power sources. As a member of the fuel cell user's group we are continuously monitoring the major development program in the US aimed at the development and demonstration of United Technology Corp's first generation (FCG-1) 4.5 MW module fuel cell power plant. This program is now underway in the

US and is sponsored by the US Department of Energy (DOE), Electric Power Research Institute (EPRI), United Technology Corp (UTC) and individual utility companies.

Other applications for fuel cells in the utility industry include: peak shaving operation, D_2 and O_2 recombination in front end electrolysis-tritium removal plants, auxiliary power sources and fuel cell powered electric vehicles for utilizing electrolytic hydrogen.

Today, fuel cells are available in a wide range of configurations, suitable for a variety of fuels and oxidants. Aqueous phosphoric acid and alkaline fuel cells are of current importance. However, major developmental and demonstration work remains to be done in each case. Component development and optimization of gas electrodes and other parts will be required if economic, efficient and reliable systems are to be produced.

The objective of this study is to review the status of development of the various fuel cell types and identify fuel cells which appear to be the most suitable for Hydro's various potential needs. Components of the various fuel cell types, which require further development, improvement, testing and demonstration have been identified for our future electrochemistry research program.

2. THERMODYNAMICS OF FUEL CELLS

A fuel cell is an electrolytic cell supplied continuously with chemical materials (stored outside the cell) which react together to provide the chemical energy for conversion to electrical energy. The direct conversion of chemical energy to electrical energy will continue to proceed in the fuel cell so long as the reactants (fuel and oxidant) are being fed into it and the products of the electrode reaction are being eliminated from the cell. The fuel cell is composed of a cathode and an anode immersed in an electrolyte, separated by a separator (Figure 1).

The anodic and cathodic reactions in the simplest hydrogen-oxygen fuel cell are:

$$H_2 \rightarrow 2H^+ + 2e^- \qquad (1)$$

$$1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^- \qquad (2)$$

$$H_2 + 1/2\ O_2 \rightarrow H_2O \qquad (3)$$

The overall reaction, Eq (3), in the fuel cell, ie, the sum of the anodic reaction, Eq (1), and the cathodic reaction, Eq (2), is the electrochemical "combustion" of H_2 and O_2 to form H_2O.

The free energy change, ΔG, of the overall reaction is related to the difference of the reversible potentials of the electrode reactions (E_r) as given by

$$\Delta G = -nFE_r, \qquad (4)$$

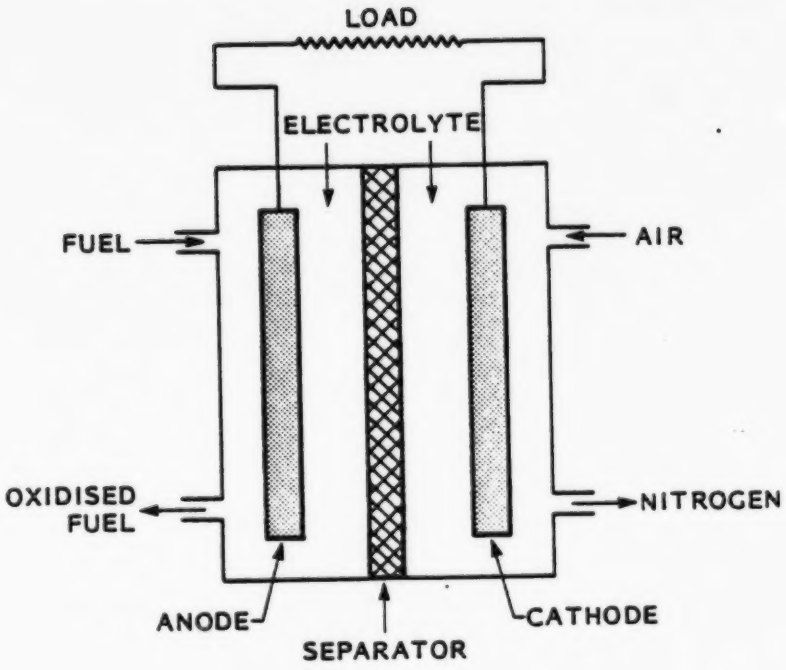

FIGURE 1
SCHEMATIC REPRESENTATION OF A FUEL CELL

where n is the number of electrons involved in the overall cell reaction, F is the Faraday constant and E_r is the reversible potential. For hydrogen-oxygen fuel cells, operating at 25°C, ΔG = -56.59 k cal/mol^{-1}, and E_r = 1.229 V. Thermodynamic data for some fuel cell reactions are given in Table I/4/.

The total energy released by a fuel cell corresponds to the enthalpy (ΔH) whereas the maximum electrical energy obtainable corresponds to the Gibbs free energy (ΔG) of the reaction. Thus, the intrinsic maximum thermal efficiency, η_i, of the cell reaction is

$$\eta_i = \frac{\Delta G}{\Delta H} . \qquad (5)$$

In the case of a hydrogen-oxygen fuel cell, ΔG = -56.69 k cal mol^{-1} and ΔH = -68.32 k cal mol^{-1} and so from Eq (5) η_i = 0.83. However, practical fuel cells operate at cell voltages in the range of 0.65-0.8 V compared to the theoretical value of 1.23 V. The thermal efficiency of an operating hydrogen-oxygen cell, therefore, ranges between 44-54%. The balance of energy is released in the form of waste heat.

The heat (Q) released from a single cell over an operating time period t is

$$Q = \int_o^t (1.48 - E_t)\ i_t\ dt, \qquad (6)$$

where E_t and i_t are the cell voltage and current respectively, at time t. For most operating cells an excess of one Watt of heat is released for every Watt of electricity produced.

The idealized current-potential curve for a low temperature hydrogen-oxygen fuel cell is shown in Figure 2. The open circuit potential is found to be about 0.2 V less than the reversible value. This loss is mainly due to the difficulty of attaining the reversible potential for the oxygen electrode. At low current densities, the cell potential drops sharply due to activation overpotential losses at both electrodes. In the linear portion of the curve, ohmic losses dominate the over-potential losses. Finally, the cell potential decreases sharply to zero when the limiting current is reached at any one of the electrodes. Under ideal conditions, when all the overpotential losses are zero, one would expect a straight line parallel to the current density axis as indicated by the dotted line in Figure 2.

TABLE I

THERMODYNAMIC DATA FOR SOME FUEL CELL REACTIONS[a,b,c]

Reaction	$\Delta G°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	n	$E_r°$, V	η_i
Temperature, 25°C					
$H_2 + 1/2O_2 \rightarrow H_2O$	-56.69	-68.32	2	1.229	0.830
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-195.50	-212.80	8	1.060	0.919
$C_2H_6 + 7/2O_2 \rightarrow 2CO_2 + 3H_2O$	-350.73	-372.82	14	1.087	0.941
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	-503.93	-530.61	20	1.093	0.950
$C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O$	-656.74	-687.99	26	1.095	0.955
$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$	-809.48	-845.17	32	1.097	0.958
$C_8H_{18}(g) + 25/2O_2 \rightarrow 8CO_2 + 9H_2O$	-1268.43	-1317.46	50	1.100	0.963
$C_8H_{18}(l) + 25/2O_2 \rightarrow 8CO_2 + 9H_2O$	-1265.87	-1307.54	50	1.098	0.968
$C_{10}H_{22}(g) + 31/2O_2 \rightarrow 10CO_2 + 11H_2O$	-1574.42	-1632.35	62	1.101	0.965
$CH_3OH(g) + 3/2O_2 \rightarrow CO_2 + 2H_2O$	-168.05	-182.61	6	1.215	0.920
$CH_3OH(l) + 3/2O_2 \rightarrow CO_2 + 2H_2O$	-167.91	-173.67	6	1.214	0.967
$NH_3 + 3/4O_2 \rightarrow 1/2N_2 + 3/2H_2O$	-85.04	-91.44	3	1.225	0.930
$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$	-143.83	-148.59	4	1.560	0.967
$C + 1/2O_2 \rightarrow CO$	-32.81	-26.42	2	0.711	1.240
$C + O_2 \rightarrow CO_2$	-94.26	-94.05	4	1.022	1.002
$CO + 1/2O_2 \rightarrow CO_2$	-61.45	-67.63	2	1.333	0.909
$Li + 1/2Cl_2 \rightarrow LiCl(g)$	-58.00	-53.00	1	2.515	1.094
Temperature 150°C					
$H_2 + 1/2O_2 \rightarrow H_2O$	-52.94	-58.142	2	1.14799	0.911
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-191.29	-191.42	8	1.03702	0.999
$C_2H_6 + 1/2O_2 \rightarrow 2CO_2 + 3H_2O$	-346.99	-340.66	14	1.07491	1.019
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	-499.54	-487.82	20	1.08324	1.024
$C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O$	-651.94	-634.29	26	1.08747	1.028
$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$	-804.98	-781.19	32	1.09099	1.030
$C_8H_{18} + 25/2O_2 \rightarrow 8CO_2 + 9H_2O$	-1263.72	-1221.70	50	1.09614	1.034
$C_{10}H_{22}(g) + 31/2O_2 \rightarrow 10CO_2 + 11H_2O$	-1569.62	-1515.37	62	1.09796	1.036
$NH_3 + 3/4O_2 \rightarrow 1/2N_2 + 3/2H_2O$	-47.28	-77.28	3	0.6835	0.612
$C + 1/2O_2 \rightarrow CO$	-36.09	-26.31	2	0.782	1.372
$C + O_2 \rightarrow CO_2$	-94.36	-94.08	4	1.02309	1.003
$CO + 1/2O_2 \rightarrow CO_2$	-58.26	-67.77	2	1.26335	0.860
$Li + 1/2Cl_2 \rightarrow LiCl(g)$	-81.38	-52.01	1	3.52942	1.565

a. Thermodynamic data are presented for the oxidation of one mole of fuel
b. 1 cal = 4.184 J
c. Table I is adapted from /4/

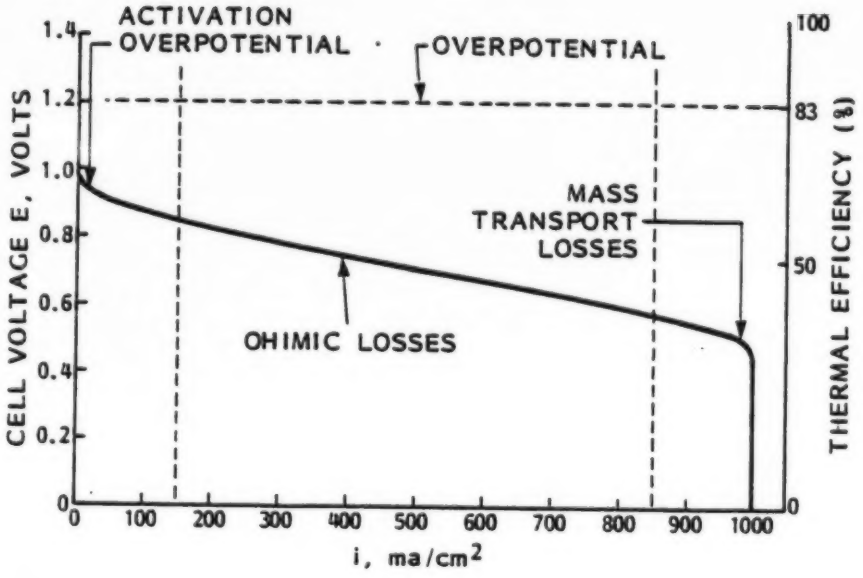

FIGURE 2

IDEALIZED CURRENT DENSITY-VOLTAGE CURVE FOR A LOW-TEMPERATURE HYDROGEN-OXYGEN FUEL CELL. ADAPTED FROM /4/

In order to attain high efficiencies and high power densities, it is essential to reduce the activation, ohmic and concentration overpotentials to a minimum. Activation overpotential of the electrodes, which is the major cause of the cell inefficiency, can be reduced by careful selection of electrocatalyst materials. A significant reduction in concentration and activation overpotentials can be achieved by using porous gas-diffusion electrodes. The ohmic component can be reduced by minimizing the inter-electrode distance, and by using highly conductive electrolytes, electrodes and current collectors.

3. CLASSIFICATION OF FUEL CELLS

Fuel cells can be classified into the following three categories, based upon operating temperature:

a) low temperature, <200°C
   - aqueous acid fuel cells
   - alkaline fuel cells
   - solid polymer electrolyte fuel cells

b) medium temperature, 500-750°C
   - molten carbonate fuel cells

c) high temperature, >1000°C
   - solid oxide fuel cells

Figure 3 summarizes the operating temperature, fuel and oxidant requirements for the most advanced fuel cell types. The general status of development of these fuel cells is shown in Table II.

In subsequent subsections the status of development of alkaline, phosphoric acid, solid polymer, molten carbonate and solid oxide electrolyte fuel cells are discussed in detail.

3.1 Alkaline Fuel Cells

Alkaline fuel cells have been developed to a sophisticated level for space applications. They operate at moderate temperatures (60-80°C) and offer high thermal efficiency (55%) and short starting time. The main limitation of these cells is the CO_2-free fuel and oxidant requirement.

Electrolyte

The electrolyte is a 25-40% aqueous solution of KOH. The conductivity of this electrolyte is high. However, the absorption of CO_2 greatly reduces the conductivity, since it replaces the highly mobile OH^- ($\lambda°$ for OH^- = 197.6 ohm $^{-1}Cm^2$) with relatively slow CO_3^{--} ($\lambda°$ for 1/2 CO_3^{--} = 69.3 ohm $^{-1}Cm^2$). Also, the build-up of CO_3^{--} in the electrolyte causes precipitation of sodium carbonate in the pores, which restricts the flow of reactant gases in the porous electrodes/13/. For these reasons CO_2 has to be kept out

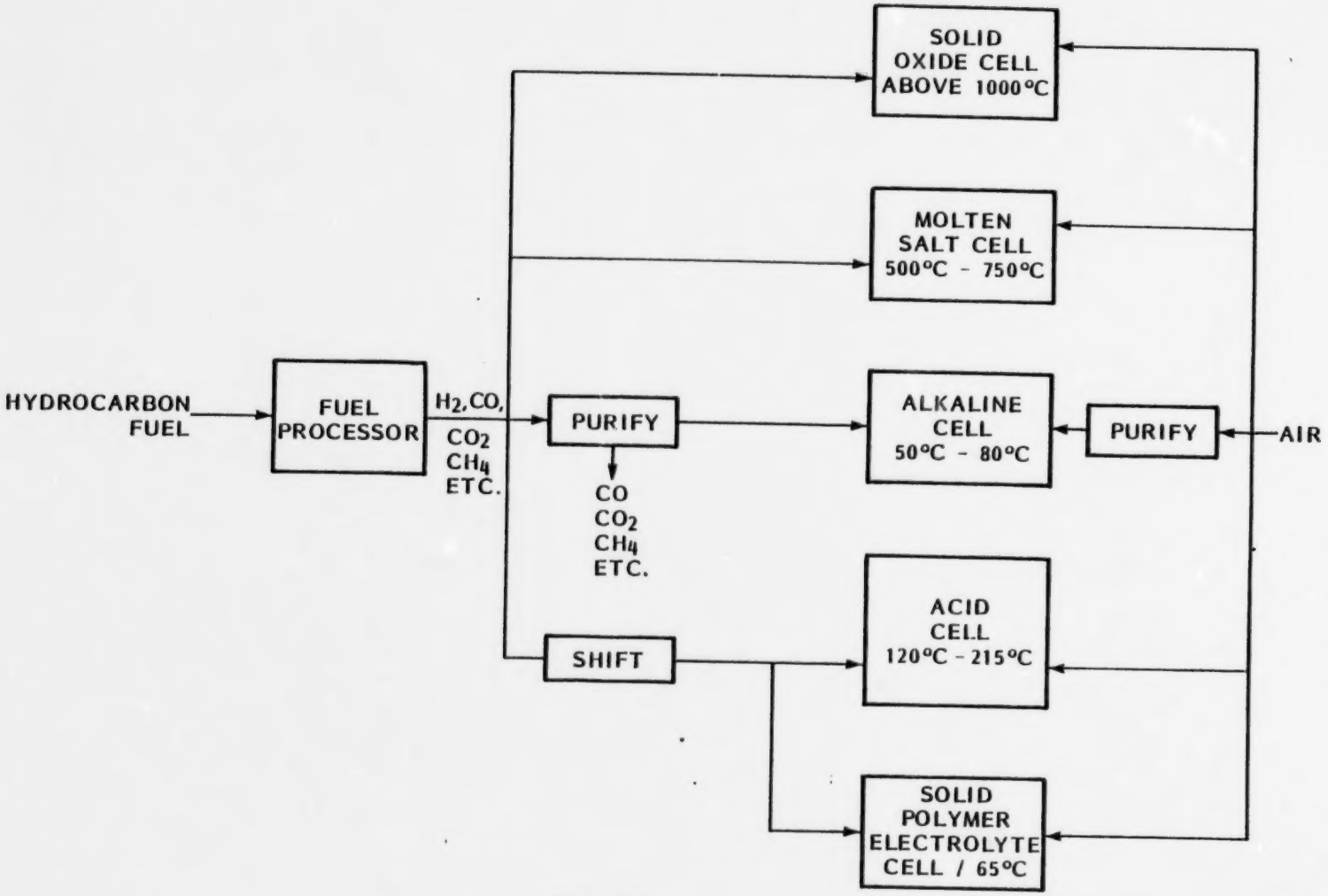

FIGURE 3

FUEL CELL TYPES

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TABLE II

STATUS OF DEVELOPMENT OF ADVANCED FUEL CELLS

Fuel Cell Type	Developer	Status of Development
Phosphoric Acid	United Technologies Corp USA	4.8 MW power plant to be tested at Con Edison, New York City, in 1982.
	Energy Research Corp, USA	2.5 kW/5/
	Inst of Gas Tech, USA	40 kW/6/
	Toshiba, Japan	15 kW/7/
	Westinghouse, USA	10 kW/8/
Alkaline	Elenco, Belgium	10 kW/9/ (Technology well developed for mass production of electrodes)
	Brookhaven National Lab, USA	0.5 kW/10/ (interest generated recently)
	Pratt & Whitney USA	12 kW/11/
	Allis Chalmers USA	15 kW/11/
Solid Polymer Electrolyte	General Electric USA	5 kW/12/
Molten Carbonate	Inst of Gas Tech USA	Approaching demonstration stage/6/
Solid Oxide	Inst of Gas Tech USA	Research stage/6/

of the cell. Alkaline cells use pure hydrogen as the fuel, and the oxidant air is freed from CO_2 by passing it through a 50% aqueous solution of NaOH/14/.

Fuel

Pure (electrolytic) hydrogen is the ideal fuel for an alkaline fuel cell. The only way to use conventional hydrocarbon fuels is to reform the fuel to a hydrogen rich gaseous fuel mixture and remove the CO_2 by scrubbing with an aqueous alkaline solution before feeding it to the cell. Since the carbon concentration (in the form of CO or CO_2) in any reformed fuel is high (eg reformed methane, CH_4, contains 1 mole of CO_2 for every 3-4 moles of H_2), scrubbing the fuel gas mixture for CO_2 removal is an expensive process/13/. Hydrazine can be used directly whereas ammonia has to be catalytically cracked prior to its use/15/.

Oxidant

Oxygen or CO_2-free air can be used as oxidant. The need to scrub air for removal of CO_2 makes the power plant complicated. Somewhat better performance is achieved by using pure oxygen instead of air, as shown in Figure 4/5/.

Anode

The most common anodes consist of a porous conductive substrate, eg carbon, on the surface of which an electrocatalyst, such as Pt or Pd, is deposited/16/. Among the low cost catalyst materials nickel appears to be a good catalyst for the oxidation of hydrogen in alkaline solutions. In order to obtain the desired porosity and high surface area, the nickel electrodes are fabricated by sintering Ni powder. Titanium containing nickel is stable and shows good electrocatalytic activity/17/. Ni_2B also appears to be a good electrocatalyst but is unstable in the operating environments/11/.

Cathode

Silver containing 11.5% Hg and doped with Bi, Ni and Ti has been successfully used as a stable catalyst for oxygen reduction/18/. An activated carbon electrode also shows good catalytic performance but carbon is known to degrade with time. Use of platinum catalyst on carbon substrate improves the life of the electrode by catalyzing the decomposition of intermediates (such as H_2O_2) of oxygen reduction. It has recently been shown that spinel $NiCo_2O_4$/19,20/ and perovskite $LaSrCoO_3$/21/ are stable and possess excellent catalytic properties.

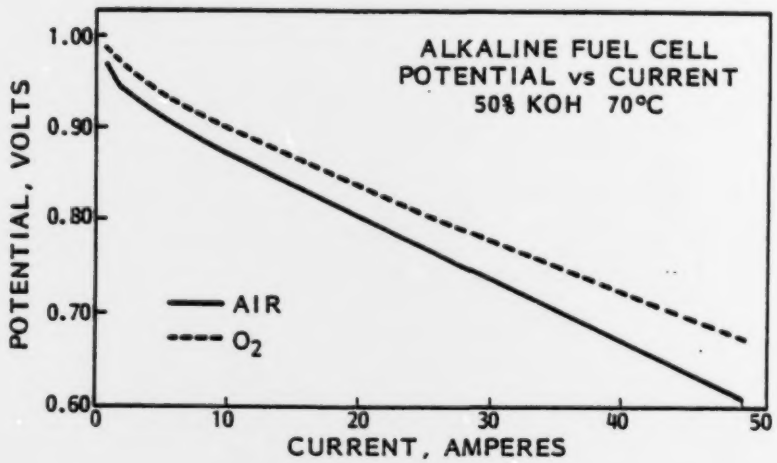

FIGURE 4

PERFORMANCE COMPARISON OF ALKALINE H_2-O_2 AND H_2-AIR FUEL CELLS. ADAPTED FROM /5/

Status of Development

During the 1960's, work on alkaline fuel cells was practically abandoned in the US in favour of acid fuel cells. However, work to improve alkaline oxygen cathodes has been continuing due to their possible applications in chlor-alkali industry and metal-air batteries. The Brookhaven National Laboratory has recently evaluated the alkaline fuel cells in light of these developments/10/. Figure 5 shows that the power output of alkaline fuel cells using advanced cathodes is much higher compared to the cathodes of 1960.

In Europe, the major emphasis has been on alkaline fuel cells since they are ideally suited to run on hydrogen fuel from non-carbonaceous resources. Table III lists materials of fuel cell components, operating and performance characteristics and developers of different alkaline fuel cells. All the fuel cells with the exception of Pratt and Whittney's high temperature, high pressure cell, operate at low temperatures (50-80°C) and yield thermal efficiencies ranging between 44-55%. All developers, except Varta AA and Pratt and Whittney, use precious metal catalysts dispersed on carbon or nickel support. Nickel based anode and cathode catalysts are also being developed at the laboratory scale but very little information is available in the open literature on the performance of these promising electrode materials in assembled fuel cells.

The most notable current work on alkaline fuel cells is being done in Belgium by Elenco NV. They have developed the technology for mass production of carbon electrodes with Pt catalyst. Fuel cells up to 10 kW using these electrodes have been tested under stationary conditions/14/. Future plans include testing these cells in electric vehicles. Their development goals include: reduction of the platinum content of electrodes from the present level of 1%, improvement of the specific power density from 60 mW/cm^2 to 125 mW/cm^2 and an increase in electrode life from 5,000 to 50,000 continuous operating hours/9/.

Varta AA has developed fuel cells using bilateral 'Janus' type electrodes fabricated on a semi-industrial scale/11/. A 500 W unit consisting of 70 cells has been tested for 9,000 hours of uninterrupted service, while electrodes in single cells have been tested for 25,000 hours.

Union Carbide's 1 kW size alkaline fuel cells using a Pt catalyst have been tested up to 5,000 hours. The system is shock resistant. The thermal efficiency of the cell is very good, up to about 500 ma/cm^2 with oxygen and about 250 ma/cm^2 with air/11/.

The Allis-Chalmers cell is based upon an asbestos capillary membrane with pores of smaller size than those of the porous electrode, to retain the KOH electrolyte. This arrangement of electrolyte allows the utilization of electrodes of a single porosity and thus avoids the difficulty of constructing electrodes

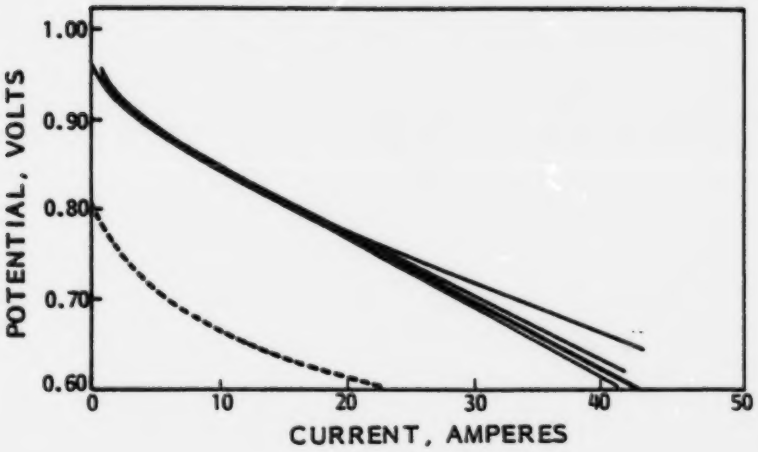

FIGURE 5

PERFORMANCE COMPARISON OF PRESENT FUEL CELLS (BOLD LINES) WITH THOSE OF 1960's (BROKEN LINE). ELECTRODE AREA FOR BOTH CELLS: 289 cm^2; TEMPERATURE: 55°C. ADAPTED FROM /10/

TABLE III

PERFORMANCE COMPARISON OF DIFFERENT ALKALINE FUEL CELLS

Developer	Fuels	Anode	Electrolyte	Cathode	Operating Parameters			Starting Time (hrs)	Stack Size	Specific Power Watt/kg	Thermal Efficiency %	Stack Life Hours	Reference
					Temp °C	Cell Voltage (V)	Current Density (mA/cm^2)						
Varta AA (West Germany)	Pure H_2	Raney Nickel	6 M KOH 1.0 mm thick	Ag on Raney Ni	60-80	0.62	250			77	42	25000	11,22
ELENCO (Belgium)	Pure H_2	Pt on C	KOH	Pt on C	60-80	0.67	80		10 kW	105	45.3	5000	9,14,15
Union Carbide (USA)	Pure H_2	Pt on Ni	6-14 M KOH	Pt on C	60	0.75	200		1 kW	35	50.7	5000	11
Allis Chalmers (USA)	Pure H_2	Pt, Pd, or Ni B on Ni	6 M KOH	Ag	80	0.8	100		10 kW	66	54.5	1000	11,15
Brookhaven National Laboratory (USA)	Pure H_2	Pd on Ni	10 M KOH	Pt on C	50-80	0.65	110	0.1	0.5 kW	88	44	-	5,10
Pratt and Whitney (USA)	Pure H_2	Ni	6 M KOH	Lithiated Nickel Oxide	200°C at 50 Atm	1-1.1	120-200		12 kW	-	67-73	-	11

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of a double porous structure/11/. The anode of sintered nickel plaque is impregnated with Pt, Pd or Ni_2B. Fuel cell stacks of up to 15 kW have been tested/15/.

Bacon/11/ developed an alkaline cell that uses 30% KOH and operates at 200°C and a pressure of 5 MPa. Pratt and Whitney Aircraft (now known as United Technologies Corporation) has modified the Bacon cell to work at atmospheric pressure but with KOH concentrations of 80-85%. The operating cell temperature is 250°C and the problem of activation overpotential is practically absent. The cell uses nickel electrodes without any noble metal catalysts and its performance is excellent. However, the use of high concentration KOH causes corrosion problems and restricts the life of the cell.

Research Opportunities

Because of short starting times and higher energy efficiencies, alkaline fuel cells are ideally suited for transportation applications, provided low cost electrolytic hydrogen stored in light weight containers is readily available. Widespread use of these fuel cells will increase the demand for electrolytic hydrogen.

The following work can be undertaken at Ontario Hydro's Research Division to lower the capital cost and improve the energy efficiency of alkaline fuel cells.

1. Develop low cost oxygen reduction catalysts such as mixed oxide catalysts of spinel and perovskite structure.

2. Improve current ratings of alkaline fuel cells by improving methods of porous nickel electrode fabrication.

3. Decrease the precious metal catalyst requirements in Elenco type electrodes by mapping the electrode for current distribution and determining the optimum catalyst requirement. Only a fraction of the catalyst is effectively utilized in present electrode designs.

3.2 Acid Electrolyte Fuel Cells

A single cell consists of a thin porous matrix containing concentrated phosphoric acid. This electrolyte matrix is sandwiched between porous carbon electrodes, catalyzed with small amounts of platinum. The cells operate at temperatures ranging from 150-215°C and produce 1-2 kW of power per m^2. The present phosphoric acid cell is nearly adequate for utility applications. The 4.8 MW demonstration plant built in New York City (Consolidated Edison) sponsored jointly by the Electric Power

Research Institute and Department of Energy, is scheduled to operate for 6,700 hours in 1982. The purity requirements on fuel and oxidant are less severe for the acid cell than for the alkaline one, so a variety of carbonaceous fuels could be utilized after reformation into a hydrogen rich gaseous fuel. However, phosphoric acid cells are vulnerable to CO poisoning, which degrades anode performance. Therefore, CO must be removed from the fuel before the gaseous fuel enters the cell.

Electrolyte

Although 85-100% phosphoric acid is the most commonly used electrolyte, it has been shown that some new electrolytes, including halogenated carboxylic acids, alkane sulphonic acids, halogenated alkane sulphonic acids and halogenated phosphoric acids/23/ can improve the impurity tolerance of anodes. If trifluoro-methane-sulphonic acid (CF_3SO_3H) is used as the electrolyte, CO can be oxidized at the Pt anode and it no longer poisons the electrode/24/.

Fuel

Although the ideal fuel for the phosphoric acid cell is pure hydrogen, reformed carbonaceous fuels such as natural gas, naphtha, coal, etc, can also be used. As discussed later, certain constitutents of reformed fuel such as CO, can have poisoning effects on the electrodes. Fuel reconditioners have been developed to minimize these problems.

Other potential fuels include ammonia and methanol. Ammonia has to be cracked at $\sim$1100°C/16/ and the resulting gases made free of ammonia before feeding it to the cell. Methanol seems quite an acceptable fuel for direct combustion in these fuel cells provided a proper catalyst is developed for its oxidation.

Oxidant

The use of air poses no problems in these cells.

Anode

Platinum is the best catalyst for hydrogen oxidation since it exhibits excellent catalytic activity. CO in the fuel gas poisons the Pt catalyst because it absorbs onto the catalyst sites. The CO content of the reformed fuel gases must be reduced by passing it through water gas shift converters to lower CO levels.

The increase in cell temperature decreases the surface coverage by CO and hence improves the tolerance for CO. However, the problem of sintering of catalyst crystallites becomes predominant at higher temperatures. (Sintering is a slow process which reduces the active surface area of the catalyst with use.)

Some new electrode materials such as phosphides, arsenides, selenides and tellurides of Fe, Co and Ni have been found to show very high exchange current densities for H_2 oxidation/13/ but none of the new catalysts has been tested for activity and stability in practical fuel cells.

Cathode

The cathode consists of porous carbon doped with small amounts of catalyst. Platinum group metals or their alloys are the only suitable catalysts since most other metals are unstable at the potential of oxygen reduction in acidic solutions. The carbon support is also attacked by the reaction intermediates such as H_2O_2. Other low cost catalysts being evaluated include carbon activated with transition metals (Mn, Fe, Co and Ni), metal chelates/13/, metal sulphides and thiospinels/25/. All these materials appear to have poor stability.

Because of low exchange current densities for O_2 reduction even at Pt group metals/13/, oxygen electrodes remain the main cause of inefficiency of present acid fuel cells.

Status of Development

The materials of construction and operating characteristics of the most advanced acid fuel cells are given in Table IV. Fuel cells using reformed hydrocarbons as fuel possess the highest specific power (66-80 W/kg) and thermal efficiency (40-45%). In addition, they offer: the ability to run on a variety of fuels, the potential for cogeneration, the most advanced technology, conventional fuel handling and simple water management. On the other hand, these cells suffer from: sensitivity of the catalysts to impurities such as CO and S, electrode degradation due to a sintering and chemical attack, requirement of a fuel reformer, requirement of precious metal catalysts and component degradation due to high temperature and acid electrolyte.

United Technologies Corp is the undisputed leader in acid fuel cells with its 4.8 MW power plant scheduled to start the final stages of testing during 1982 at Consolidated Edison in New York City. Other organizations involved in acid fuel cell development are the Energy Research Corporation, Westinghouse and Engelhard.

The current trend in phosphoric acid fuel cells is to improve efficiency and power density by operating at higher temperatures (up to 215°C) and pressures (up to 300 kPa). The effect of temperature and pressure on cell performance is shown in Figure 6. It is evident that significant gain can be made by pressurization. The higher temperatures deteriorate the life of the cell due to sintering of the electrocatalyst. Current platinum catalyst loading is 0.5 mg/cm^2, which is not effectively utilized. Future goals include reduction of the platinum content of the electrode.

TABLE IV

PERFORMANCE COMPARISON OF DIFFERENT ACID FUEL CELLS

Organizations Involved	Fuel	Anode	Electrolyte	Cathode	Operating Parameters: Temp (°C)	Operating Parameters: Cell Potential (Volts)	Operating Parameters: Current Density (mA/cm²)	Starting Time (hrs)	Stack Size	Specific Power of Stack Watts/kg	Thermal Efficiency %	Stack Life Hours	Reference
UTC (water cooled) ERC (air cooled) Westinghouse (air cooled) Engelhard	H_2, reformed hydrocarbons, methanol and synthetic gas	0.5-2 mg/cm² Pt on C	85-100% H_3PO_4	0.5-2 mg/cm² Pt on C	170-190	0.6-0.7	150-85	3 /5/	4.8 kW Tests planned for 1982	66-80	40-45	-	5
	Direct CH₃OH	5-10 mg/cm² Pt on C	H_3PO_4 or HF	Pt on C	105-150	0.6	60	-	Laboratory cell	22	52	-	26
	Direct methanol	20-40 mg/cm²	H_2SO_4	Pt-Ru	70	0.4	50	-	Laboratory cell	15	32	1000	27

UTC - United Technologies Corporation
ERC - Energy Research Corporation

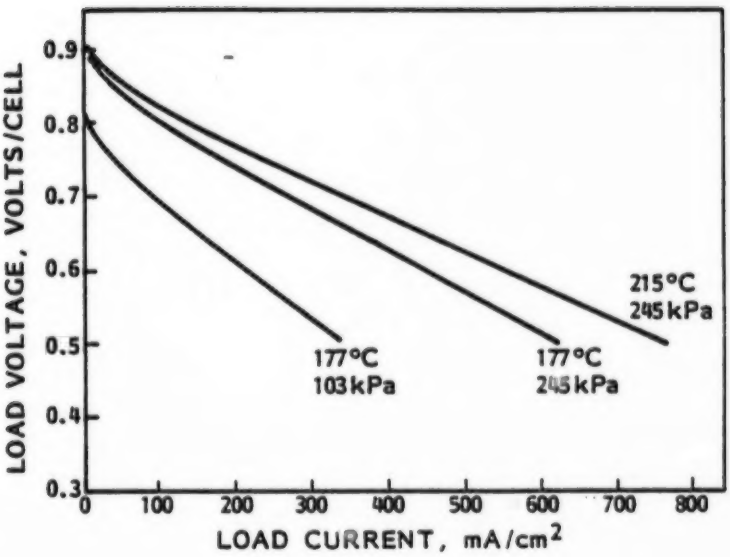

FIGURE 6

EFFECT OF TEMPERATURE AND PRESSURE ON CELL PERFORMANCE OF PHOSPHORIC ACID CELL ADAPTED FROM /5/

The direct liquid petroleum gas-air fuel cell offers a simpler power system than fuel cells using reformed hydrocarbons, but the efficiency of these cells is very low. Improvements in efficiency and specific power seem possible if a concentrated effort is made to develop a suitable electrocatalyst. Recently, Adams and Barger/24/ have shown that the electrolyte plays an important role in hydrocarbon oxidation. For example, the exchange current density for propane oxidation on Pt in CF_3SO_3H is considerably higher than in phosphoric acid, as shown in Figure 7. The limiting current density in CF_3SO_3H is about 15 times larger than that in 85% H_3PO_4.

Direct methanol-air fuel cells appear ideal for electric vehicles. However, there is little work in progress in this direction. Complexity and the slowness of the methanol oxidation reaction are cited as the main problems in this type of fuel cell/13/. Current interest in electro-organic chemistry could lead to the development of better electro-catalysts. Recent work/28,29/ has shown that incorporation of Ru, Sn and Mo into Pt catalysts enhances the methanol oxidation. Other catalysts that promote oxidation of methanol and its intermediates have also been identified/13/. However, oxidation of methanol in the cathode chamber increases the cathode polarization. Use of solid polymer electrolyte membrane should reduce the diffusion of methanol and improve the voltage output. Sumitomo Corporation in Japan is working on such an improved cell/30/.

Research Opportunities

Phosphoric acid fuel cells are capable of running on a variety of fuels with an energy efficiency of 40-45%, considerably higher than other energy conversion devices. With the level of government and industrial backing in the US, they are bound to find application for power generation. Improvements in cell life and lowering of cell costs are necessary to improve the cost competitiveness of these cells with other methods of power generation. The following work can be undertaken at the Ontario Hydro Research Division to make these improvements:

1. Development of non-noble electrocatalysts for H_2 oxidation and O_2 reduction.

2. Studying the mechanisms of sintering in existing phosphoric acid fuel cells. This can lead to improved methods of electrode fabrication. Experiments have shown that sintering effects can be greatly minimized by alloying or choosing appropriate supports on which the surface mobility of the atoms and crystallites of the catalyst is minimum/11/.

3. Evaluation of new electrolytes such as halomethane sulphonic acids, for use in fuel cells in order to improve the CO tolerance of the cell.

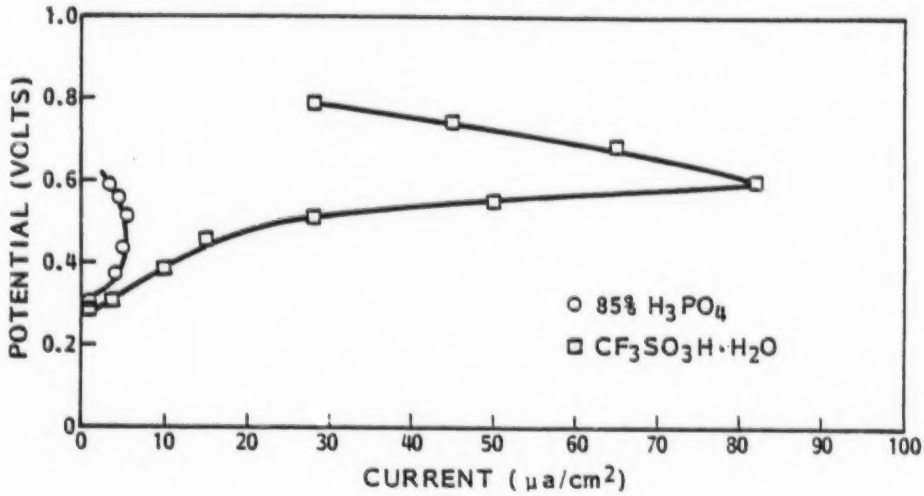

FIGURE 7

CURRENT DENSITY-POTENTIAL DIACRAM COMPARING THE ELECTROCHEMICAL OXIDATION OF PROPANE ON SMOOTH PLATINUM AT 135°C IN $CF_3SO_3H \cdot H_2O$ AND IN 85% H_3PO_4 ADAPTED FROM /24/

4. Conducting a detailed study of current and potential distribution on porous electrodes to find the optimum platinum catalyst requirements. Only a fraction of the Pt catalyst is effectively utilized in present fuel cells.

5. Developing a direct methanol-air fuel cell with an efficient electrocatalyst and Nafion as the separator material. The resulting cell could be ideal for transportation, provided acceptable specific power density can be achieved.

3.3 Solid Polymer Electrolyte (SPE) Fuel Cell

The potential for developing an SPE fuel cell was first realized in the late 1950's but the developments were so fast that by 1965 an SPE fuel cell was used as a power source in the Gemini Spacecraft. In fact, an SPE fuel cell was among the first fuel cells used in an engineering application/31/.

SPE fuel cells have been developed by General Electric Co who have been pursuing their development since the 1960's under the sponsorship of NASA, US Air Force, ERDA and others. A schematic diagram of General Electric's SPE fuel cell is shown in Figure 8. A hydrated cation exchange membrane (Nafion) serves as the separator, electrolyte and support for electrocatalysts. The fine particles of the anode and cathode catalysts are embedded on the two sides of the membrane. As a result, the cell design is compact and is simple to fabricate. The high performance of SPE fuel cells is made possible by the high surface area of the catalysts and the small internal resistance of the cell.

Electrolyte

Several ion exchange membranes have been developed for use as electrolytes in these fuel cells. The properties of these membranes are compared in Table V. General Electric's present technology uses Nafion membranes, a sulphonated analogue of Teflon:

$$CF_2 - \underset{\displaystyle (SO_3H)\ (H^{\cdot} \times H_2O^{+})}{\overset{\displaystyle CF_3}{\overset{|}{CF}} - CF}$$

Nafion is extremely stable in the fuel cell environment and exhibits excellent physical and electrochemical properties while wet or dry in the temperature range of 25-125°C. Nafion films of 0.12 - 0.5 mm thickness have been used/32,33/, the minimum thickness being dictated by the differential pressure across the membrane.

Maintaining the proper moisture content in the polymer is the key to successful operation of the cell. In order to maintain proper water content, it is necessary to have water vapour pressure in both the reactants at least equal to the saturation vapour pressure for the particular operating temperature of the cell/31/.

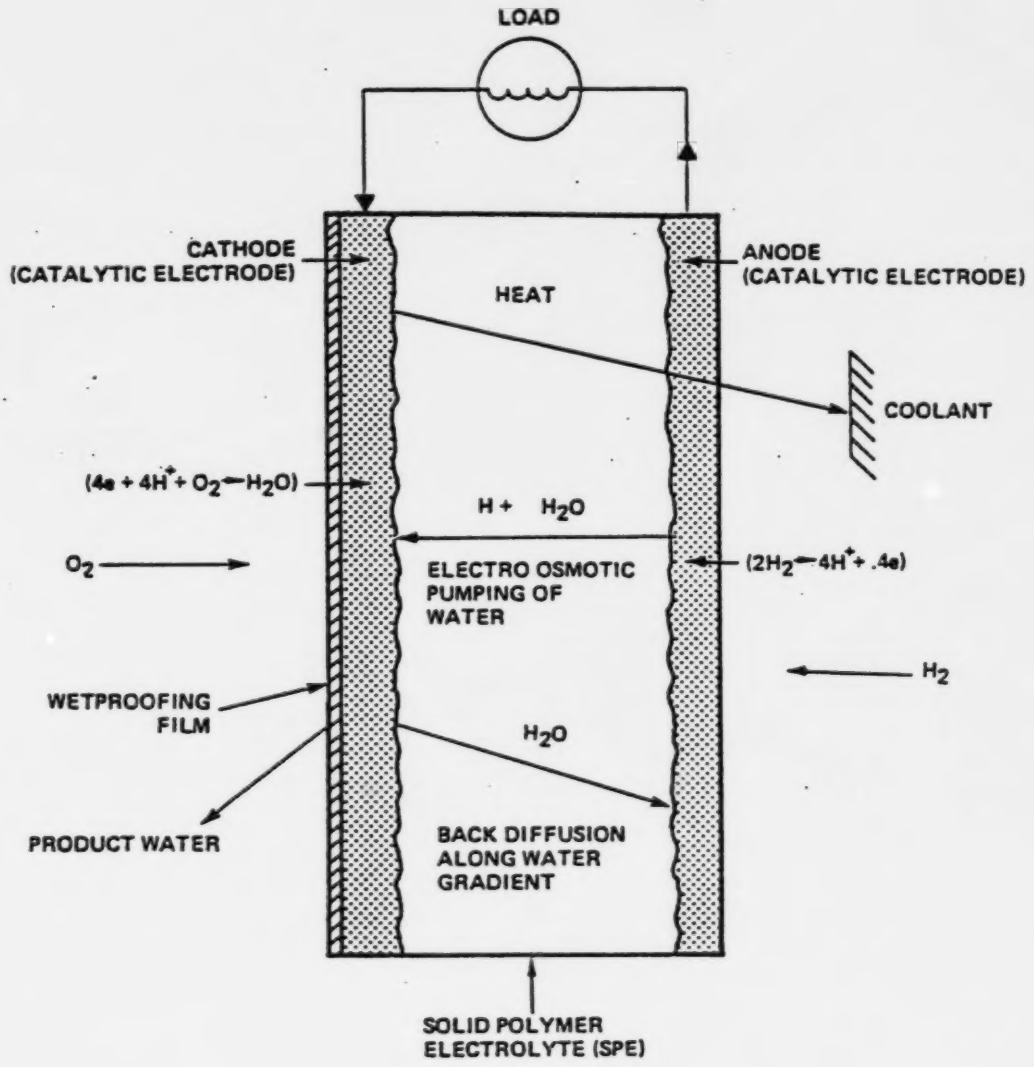

FIGURE 8

A SCHEMATIC DIAGRAM OF
THE SOLID POLYMER ELECTROLYTE FUEL CELL

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TABLE V

PROPERTIES OF ION EXCHANGE MEMBRANES[a]

Property	Desired	Phenol Sulphonic	Poly-styrene Sulphonic	Poly-trifluoro-styrene Sulphonic	Per-fluori-nated Sulphonic
Ionic Resistivity (25°C) (ohm-cm)	≥ 20	100	≤ 20	≤ 20	≤ 20
Ionic Resistance (25°C) (ohm-cm)	≥ 0.7	10	≤ 0.7	≤ 0.7	≤ 0.7
Hydrogen Permeability (25°C) (cm^3/m^2-hr-atm)	≥ 20	≤ 20	≤ 20	≤ 20	≤ 20
Mullin Burst Strength (25°C) (kPa)	> 345		1035	207-276	517-690
Tensile at Break (25°C) (MPa)	>13.8	Controlled by Cloth	20.7	6.2	13.8-20.7
Elongation at (25°C) (per cent)	> 100		100	40	> 100
Maximum Temperature of Thermal/Hydrolytic Stability	> 100°C	50°C	> 100°C	> 150°C	>150°C
Oxidative Degradation after 18 Hours exposure to 80°C, 30% H_2O_2, 20 ppm Fe^{+2} (per cent polymer degraded)	< 1	100	100	< 1	< 1
Crease/Crack (Ability to withstand 5 folds after 100°C drying)	Pass	Fail	Pass	Fail	Pass

a: Adopted from/32/

Fuels

Most SPE cells tested use pure hydrogen as the fuel. However, some work has been directed towards the use of low calorie gas and reformed fuels as the source of hydrogen. It was found that the existing anode catalysts operating at 74°C are poisoned by CO/5/. Therefore, CO has to be eliminated from the fuel by methanation or oxidation. Since CO_2 is inert in the system, CO_2 containing fuel can also be used/15/.

Oxidant

Pure oxygen has been used as an oxidant in the space applications of SPE fuel cells. Studies conducted with air have shown that its use does not decrease the performance of the cell/33/.

Use of a chlorine oxidant yields higher energy conversion efficiencies due to the reversible nature of the Cl_2 electrode. An H_2/Cl_2 fuel cell forms a part of the rechargeable H_2/Cl_2 electrochemical storage system with electric to electric (ETE) system energy storage efficiencies greater than 70%/32/.

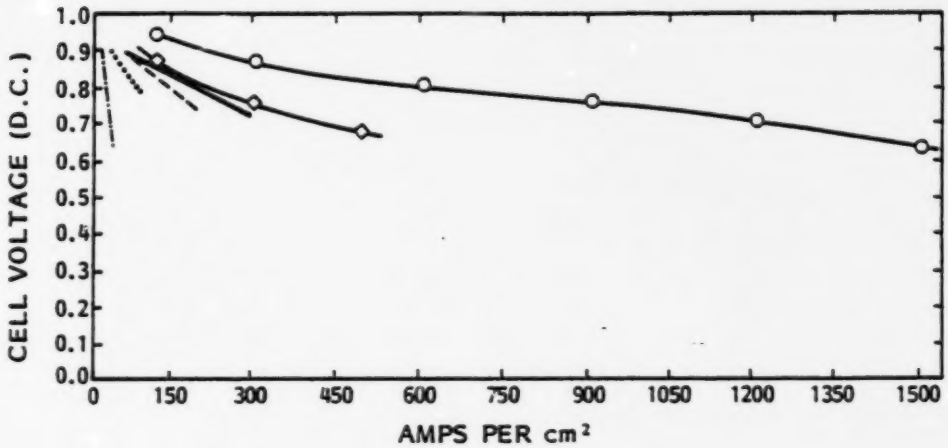
Electrodes

General Electric uses a very thin layer of precious metal electrocatalyst (mainly Pt) bonded and embedded into the surface of the membrane on both sides. Conductive collectors of Ti, in the form of screens, ribs, etc, contact the hydrocarbon bonded catalytic electrodes and provide current and gas distribution. The collectors need not be electrochemically active but they are lightly coated with noble metal to minimize contact resistance and allow invariant performance at high current densities. The oxygen cathode is wet proofed with an electrically conductive coating to prevent masking of the catalyst with the product water.

Status of Development

During the 60's and early 70's, a major emphasis in the SPE fuel cell technology was directed towards cell life at practical operating temperatures. A performance of over 40,000 hours at 82°C and 1075 A/m^2 was demonstrated/33/. The emphasis was then switched to the optimization of performance levels. Figure 9 shows the improvement achieved during 1965-76/33/. The rated performance for the present SPE cells is 12,900 A/m^2 at 0.7 V compared to 430 A/m^2 at the same voltage for the Gemini SPE fuel cell/33/.

It is claimed that there are no known size limitations on scale up and that considerable cost savings/unit area are realized in the manufacture of large size cells. Single cells with an electrode area of 0.14 m^2 (1.5 ft^2) have been fabricated/31/ but complete systems of up to 5 kW have been produced using smaller electrodes/31/.



1965 GEMINI
1969 BIOSATELLITE
1973 SPACE SHUTTLE TECHNOLOGY
1974 NASA LRC
1975 NASA TECHNOLOGY ADVANCEMENT PROGRAM
1976 NASA TECHNOLOGY ADVANCEMENT PROGRAM

FIGURE 9

PERFORMANCE GROWTH IN H_2/O_2 SPE FUEL CELLS

SPE fuel cells have been developed for special applications such as space applications/31/. A few studies were directed towards incorporation of the SPE fuel cell technology into ground powered vehicles using reformed fuels. A 5 kW SPE system concept that operates at near ambient pressure with reformed methanol has been found to be feasible/5/. Removal of CO from the fuel gas stream, however, is necessary to avoid poisoning of the anode catalyst. Development of new electrocatalysts with greater tolerance for CO is necessary to make the SPE fuel cells suitable for general applications where use of impure hydrogen from reformed hydrocarbon fuels is more acceptable.

Direct methanol-air fuel cells with solid polymer electrolytes/30/ suitable for a variety of mobile and stationary applications are being developed in Japan by Sumitomo Corporation. No details of their work are available.

The hydrogen/chlorine regenerative SPE fuel cell concept has been tested by General Electric/31/ and a schematic of the 5 kW conceptual system is shown in Figure 10. The power plant is being evaluated for automotive use. If further developed, this energy efficient system might find application in the utility industry.

Research Opportunities

1. Development of new non-noble metal catalysts to improve the cost competitiveness of SPE fuel cells. For example, certain forms of PbO_2 may find application as oxygen reduction catalysts.

2. Reducing the precious metal content of catalyst layers by developing mixed metal and metal oxide catalysts for anodes and cathodes respectively.

3. Reducing the thickness of precious metal coatings on the current collector, while minimizing the contact resistance.

4. Conducting an in-depth study of the critical parameters for scale-up of SPE fuel cells. This could help produce large systems without the problems of local overheating, membrane drying and pinholing/11/.

5. Developing or monitoring the developments of regenerative SPE fuel cell systems, such as the H_2/Cl_2 system. With high ETE energy efficiencies, these cells could be of direct interest to utilities.

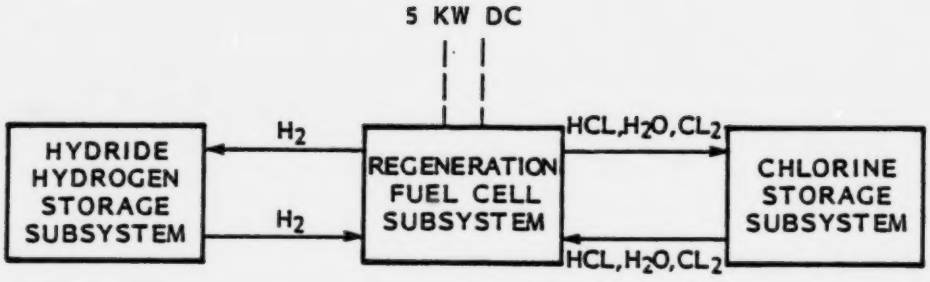


FIGURE 10

5 KW SPE H_2/CL_2 FUEL CELL SIMPLIFIED SCHEMATIC DIAGRAM

3.4 Molten Carbonate Fuel Cells (MCFC)

In the 1940's molten carbonate was first used as an electrolyte for fuel cells/11/ and until the 1970's only scattered work was carried out on this type of fuel cell. Early work on molten carbonate cells revealed that they operate at high efficiency and the material cost is low. They are well suited for cogeneration and are capable of oxidizing hydrocarbons including natural gas directly without any external reformation. A major program was initiated in the 1970's to investigate this fuel cell system. Present cells operate at 500-750°C and offer an energy efficiency of 54% at a 100 mA/cm^2 current density.

The operation of the MCFC is schematically shown in Figure 11. Oxygen reacts with CO_2 to form $CO_3^=$ which migrates through the electrolyte to the anode where it is converted to carbon dioxide after reaction with hydrogen.

Electrolyte

Binary and ternary mixtures of Li_2CO_3, Na_2CO_3 and K_2CO_3 are used as electrolytes, which have melting points in the range of 500-750°C. Based upon the method of molten electrolyte containment, MCFC's are divided into the following three categories:

a) Matrix cell - the electrolyte is held within a porous sintered magnesia diaphragm.

b) Free electrolyte cell - the electrolyte is held between electrodes.

c) Paste electrolyte - the electrolyte is formed into a stiff paste with magnesia powder.

Internal resistance of the molten electrolyte limits the cell power output. Ohmic drop across the electrolyte can be reduced by reducing the thickness of the electrolyte and/or by increasing the porosity of a magnesia diaphragm, if one is used. In addition to the internal resistance, discontinuous contacts of the electrode with the electrolyte also contribute to the resistance of the cell.

Anodes

Porous anodes of nickel, stainless steel, stainless steel with iron-iron oxide mixtures, lithiated manganous oxide and lithiated nickel oxide have been used/34/. Due to the high operating temperature of the cells, no activation polarization is found even at high current densities. Porous stainless steel anodes with oxide coatings appear to perform better for hydrogen oxidation in the presence of CO/34/.

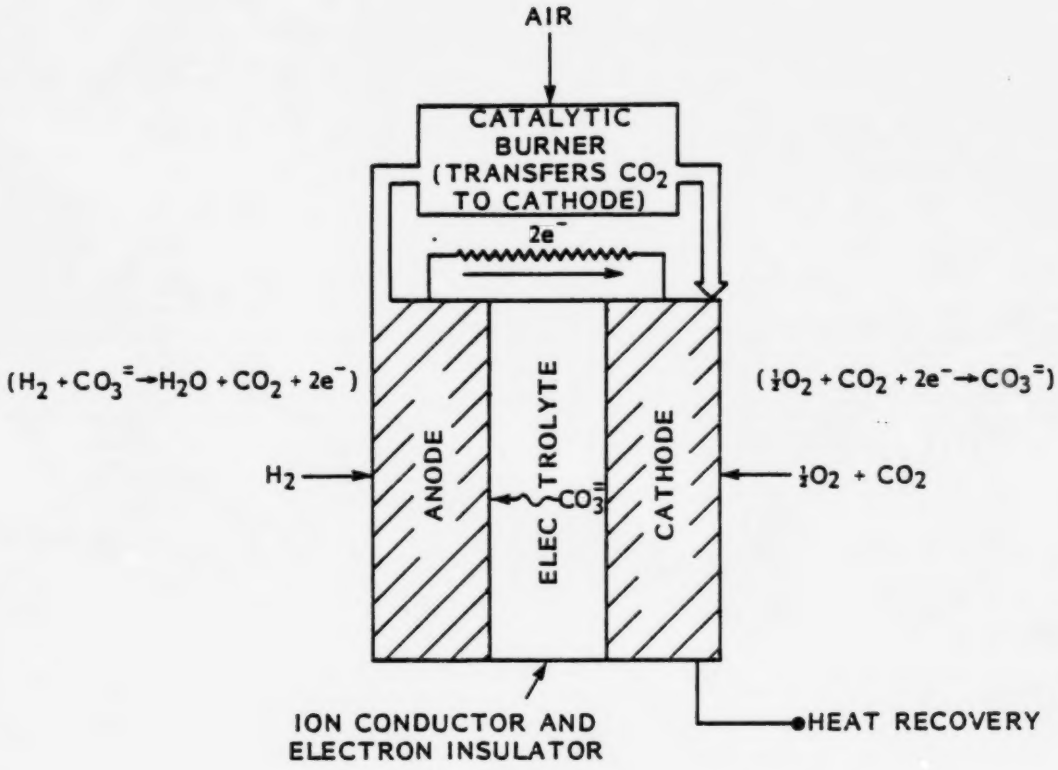


FIGURE 11

SIMPLIFIED SCHEMATIC OF MOLTEN-CARBONATE FUEL CELL ADAPTED FROM /6/

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Due to high CO tolerance, the fuel processor is simple. It is also possible to build molten carbonate fuel cells that do not require external fuel reformers since the reforming can occur within the cell/11/. Such cells contain a double duty anode consisting of two parts: fuel is reformed in one part before being oxidized in the second part of the anode. In the case of some fuels, a commercial reformer operates at higher temperatures than does the molten carbonate cell. A large electrode area, and slower throughput per unit area, can make internal reforming efficient/11/.

Cathodes

Stainless steel, nickel, silver, lithiated nickel oxide and mixtures of copper and copper oxide have been used as electrocatalysts for O_2 reduction/34,35/. Silver cathodes appear to be unstable. Thus, the present trend is to use lithiated nickel cathodes. With high surface area cathodes fed with O_2 or air containing CO_2, activation polarization is found to be virtually absent/36/.

Status of Development

United Technologies Corporation, General Electric, Energy Research Corporation and Institute of Gas Technology are involved in the development of molten carbonate fuel cells. While most of the work has been done on laboratory scale cells, operation of a 1 m^2 single cell has been reported recently/37/. Extensive stack test information and data are still lacking and numerous material problems outlined below, remain to be solved for each component of the cell.

a) Electrolyte Evaporation: Due to the difference in the rate of evaporation of the electrolyte components, the composition of the electrolyte changes with time (eg in a Li_2CO_3 and K_2CO_3 mixture, Li_2CO_3 evaporates more rapidly). As a result, the resistance of the electrolyte and the contact resistance increase. Figure 12 shows that the terminal cell voltage at 100 mA/cm^2 decreased with time whereas the iR free cell voltage changes only slightly/36/. Thus, this loss is a major life limiting factor for molten carbonate fuel cells/38/. Studies are being conducted to identify the mechanism of vapourization and reduce the vapour loss by: operating the fuel cell at elevated pressures, reducing the operating temperature and optimizing reactant compositions/37,38/.

b) Sintering of the Anode: At the operating temperatures of the molten carbonate fuel cells (500-750°C), the electrode materials sinter rapidly. The result is that the active surface area of the anode is reduced and the pores are blocked. To prevent cell deterioration, the sintering resistance of the anode has to be increased. Dispersion of fine inert particulates such as MgO and Al_2O_3 is being studied as a means of increasing sintering resistance/39,40/. The presence of Cr in the NiO anode has been shown to help the sintering resistance.

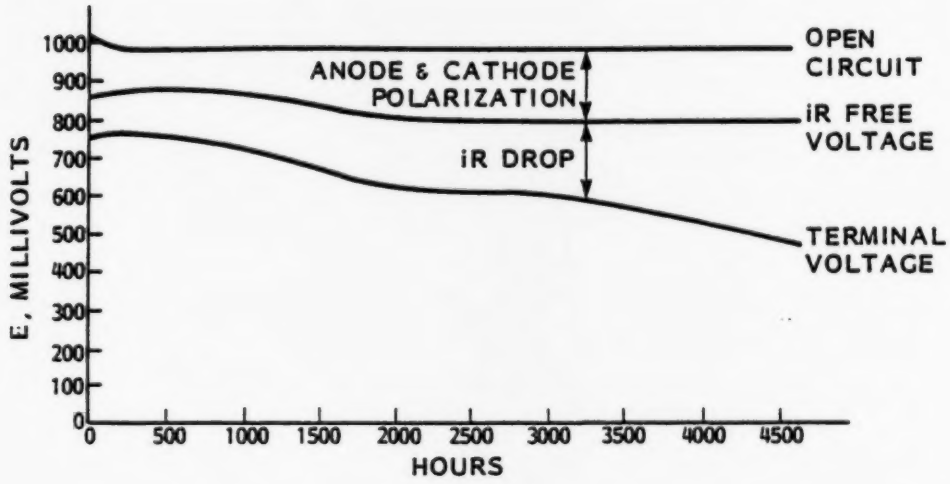

FIGURE 12

PERFORMANCE OF MOLTEN CARBONATE FUEL CELL
AT A CURRENT DENSITY OF 100 mA/cm^2

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c) Cathode Instability: Most cathode materials tested have been found to be unstable at the operating potentials of the oxygen cathode/41/. NiO, the most commonly used cathode, has a tendency to dissolve in the electrolyte. The Ni^{2+} ions travel towards the anode where they get reduced/41/. This obviously limits the life of the cathode as well as the anode. As a result, new cell designs and more stable catalyst materials are being developed to solve this problem/41,42,43/.

d) Carbon Deposition at Anode: The following side reactions occur at the anode and result in the formation of carbon deposits at the anode:

$$3CO_2 + 4e \rightarrow C + 2CO_3^{2-} \quad (7)$$

$$3CO + 2e \rightarrow 2C + CO_3^{2-} \quad (8)$$

$$CO + CO_2 + 2e \rightarrow C + CO_3^{2-} \quad (9)$$

3.5 Solid Oxide Electrolyte Fuel Cells

Certain mixtures of oxides exhibit a rapid increase in conductivity with a rise in temperature. The solid electrolyte cells use such solid ceramic oxide electrolytes and operate at temperatures of about 1000°C.

At the cathode, oxygen is reduced to an oxide ion as shown in the reaction:

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (10)$$

The oxide ions migrate through the electrolyte via anion defects to the anode where they react with hydrogen according to the reaction:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (11)$$

At operating temperatures of about 1000°C, the cathodic and anodic reactions proceed practically free of activation polarization and energy efficiencies as high as 54% at a current density of 100 mA/cm^2 have been demonstrated. Because of the absence of any liquids, there is no problem of maintaining a stable three phase interface. The cell is tolerant to CO which makes the fuel processor simpler.

High temperature waste heat can be utilized for the coal gasification process/11/ to provide fuel gas for the fuel cells. Internal fuel processing of methane seems to be possible/44/. The technical realizability and economic use of these fuel cells depends upon successful solution of all problems of technology and materials arising from the high operating temperature.

Electrolyte

A suitable solid electrolyte should have high O^{2-} conductivity, negligible electron conductivity, phase stability, mechanical strength, gas tightness, thermoshock stability, chemical resistance to reaction gases and compatibility with the electrode and interconnection materials/45/. These requirements are sufficiently satisfied by ceramic solid electrolytes of doped zirconia, such as: $(ZrO_2)_{0.85}(CaO)_{0.15}$, $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ and $(ZrO_2)_{0.92}(Y_2O_3)_{0.04}(Yb_2O_3)_{0.04}$.

Electrodes

The suitable electrode materials should be of moderate cost, possess good adherence for electrocatalyst (if one is used), be chemically inert, be electrochemically active for the electrode reaction, possess compatible thermal expansion, and low resistivity. Pt, Co, Ni and ZrO cermet stabilized Co or Ni have been used as anode materials to date/46/. Promising cathode materials include Pt, $LaCoC_3$, $LaCoO_3$ containing Sr, $PrCoO_3$, In_2O_3 containing Sn, $LaNiO_3$ containing Bi, $LaMnO_3$ containing Sr and SnO_2 containing Sb/46/. Although some single cell data at 1000°C are available on these electrode materials, the long-term performance of the electrodes with real fuels in multiple cells remains to be demonstrated. The suitability of Pt as electrode material has already been questioned due to its tendency to evaporate and react with oxygen and zirconia/46/.

Status of Development

The solid oxide fuel cells, being developed at laboratory scale /6/, are energetically efficient and have the potential to be the heart of a very fuel efficient, integrated power plant system for base load generation of electricity from coal/47/.

However, an immense effort is required before the material and technological problems can be resolved. Some of the problems have been identified as: lack of a suitable interconnection material compatible with electrolyte, electrode and other cell components/48/; carbon deposition at the anode/49/; cracking of cells due to thermal expansion mismatching/49,50/; change in the nature of electrodes due to sintering/49/; instability of zirconia electrolyte/46/ and non uniform current distribution resulting from small three-phase interfacial areas or high resistivity of oxide cathodes/49/.

The most notable work on solid electrolyte fuel cells has been conducted at Westinghouse. They have assembled a battery of 20 cells of electrode area 2 cm^2/cell. $(ZrO_2)_{0.9}(Y_2O_3)_{0.1}$ electrolyte (0.04 cm thick) separates the two porous Pt electrodes. The performance of a Westinghouse 3 cell unit is shown in Figure 13. The slope of the current potential curve corresponds approximately to the resistance of the electrolyte layer, indicating that a further improvement in performance is possible by reducing the thickness of electrolyte.

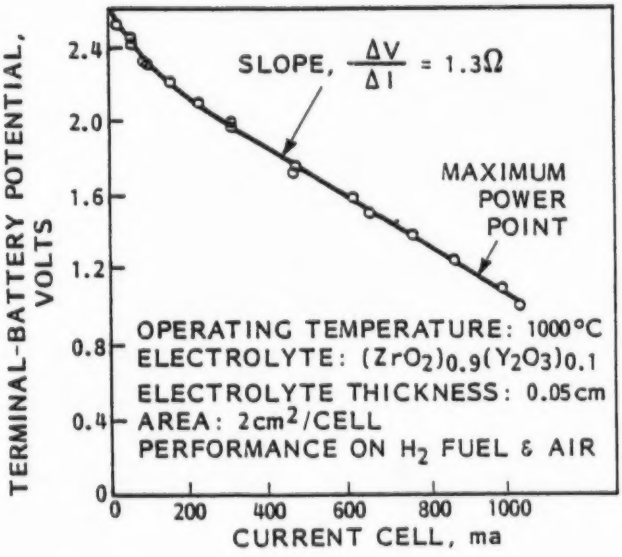

FIGURE 13

THE PERFORMANCE OF A WESTINGHOUSE 3-CELL HYDROGEN-OXYGEN FUEL CELL BATTERY. ADAPTED FROM /11/

4. APPLICATIONS OF FUEL CELLS

The applications of fuel cells depend not only upon their electrochemistry and engineering design but also upon the relative economics of the operation of cells in competition with other sources of power. Since different applications can tolerate different levels of cost and performance, each type of fuel cell may not be ideal for every application. Operating characteristics and projected applications of the different fuel cell types are given in Table VI.

4.1 Power Generation

The characteristics of fuel cell power plants suitable for centralized and decentralized power generation are shown in Table VII/51/. In order to be competitive with other methods of power generation, the systems should also have low capital cost, high thermal efficiency, long operating life, possibility of cogeneration and short lead and starting times.

Phosphoric acid fuel cells (PAFC) meet most of the above criteria and they appear to be the most suitable for power generation in the near term (10 years). Since low temperature waste heat can be utilized for space heating in residential and commercial buildings, PAFC's could find long range application in decentralized generation in residential and commercial buildings. Lowering capital cost (by lowering of precious metal content of electrodes), improving the CO tolerance and increasing the operating life of the cells are, however, necessary to improve the cost competitiveness of the system.

Molten carbonate and solid oxide fuel cells are highly efficient because of the absence of any activation overpotential losses. They generate high temperature waste heat and are best suited for cogeneration. Cell components are made of low cost materials and the fuel reformers are simple. They appear to be the best technologies for centralized and decentralized generation. Both these technologies are in the early stages of development and are likely to replace PAFC's as second and third generation cells as the material problems are resolved.

Alkaline fuel cells are inflexible to fuels other than pure hydrogen and thus may not see any use in power generation. SPE solid polymer electrolyte cells have high capital costs due to the high cost of the membrane and the catalyst.

4.2 Peak Shaving

The off peak power stored as hydrogen could be used to generate power using fuel cells during the peak demand periods. A hydrogen/oxygen power storage system for this purpose would consist of an efficient low cost water electrolyzer, a low cost bulk hydrogen storage system and an efficient fuel cell meeting all criteria outlined for power generation.

TABLE V:

OPERATING CHARACTERISTICS AND PROJECTED APPLICATIONS OF DIFFERENT FUEL CELL TYPES

Fuel Cell Type	Alkaline	Acid		SPE	Molten Carbonate	Solid Oxide
		Reformed Fuel	Direct Organic Fuel			
Status of Development	Advanced to 15 kW units	Advanced to 40 kW units	Laboratory Studies	Developed to 5 kW units	Laboratory Scale	Laboratory Studies
Capital Cost	High, (possibility of lowering)	High	High	High	Low	Low
Main Contributors to Capital Cost	Pt catalyst	Pt catalyst, reformer	Pt catalyst	Pt catalyst, separator, reformer	-	-
Fuels	Pure hydrogen	H_2 and all reformed organic fuels	Partially oxidized hydrocarbons (eg methanol)	H_2 and all reformed organic fuels	H_2 and organic fuels	H_2 and organic fuels
Reformer Requirements	Not applicable	Reformer and shift converter	None	Reformer and shift converter	Internal reforming possible	Internal reforming possible
Oxidant	O_2 or CO_2 free air	Air	Air	Air	Air	Air
Operating Temperature	50-80°C	120-215°C	25-150°C	65°C	500-750°C	1000°C
Suitable for Cogeneration	No	Yes	No	No	Yes	Yes
Starting Time (mins)	6	180		5	(large)	(large)
Energy Efficiency (%)	42-55 @ 100 mA/cm^2	40-45 @ 200 mA/cm^2	32-55	54% at 100 mA/cm^2	54% at 100 mA/cm^2	53% at 100 mA/cm^2
Stack/Operating Life (hrs)	5,000 /9/	-	1,000	40,000	-	-
Energy Density						
W/kg	110 /9/	66-80 /5/	15-22 (25,26)	-	-	-
Projected Applications	Transportation, Auxiliary Power, D_2-O_2 combination	Centralized generation, decentralized residential and commercial generation	Transportation	Transportation, D_2-O_2 combination, Auxiliary power	Centralized generation Industrial generation	Centralized generation Industrial generation

TABLE VII

FUEL CELL POWER PLANT CHARACTERISTICS

Characteristics	Benefits
. Modular Size . Short lead time	. Minimize financial impact . Better capacity/load match . Enhance planning flexibility
. Low emissions/water use . Truck transportable	. Broad siteability
. High efficiency - 8.7×10^6 J/kWh at 100% FL - 9.5×10^6 J/kWh at 50% FL	. Fuel conserving
. Unmanned operation	. Minimize operating costs
. Dispersed siting	. Decrease transmission line losses . Defer transmission line construction
. Waste heat recoverable	. Cogeneration application
. Factory manufactured	. High quality control
. Multiple fuels - Distillates, methane, LPG, coal-derived fuels, hydrogen - Retrofittable	. Use today's fuels today . Switch to coal-derived tomorrow
. High availability (85-90%)	. Reduced reserves
. Load following	. Enhance operation flexibility . Improve system operations . Provide spinning reserve

All combinations of known water electrolyzer-fuel cell technologies yield electric to electric (ETE) system efficiencies much lower than that possible with pumped water storage systems (~95%)/52/. Hydrogen/oxygen storage systems based upon alkaline and solid polymer electrolyte yield ETE efficiencies of only 40%. Efficiencies up to 60% seem possible with solid oxide electrolyte systems.

SPE based H_2/halogen storage systems appear to be promising compared to all H_2/O_2 systems. Figure 14 shows that ETE efficiencies in excess of 70% have been demonstrated at current densities of 220 mA/cm^2 and ambient temperature and further improvements are projected to improve system efficiencies to 80%/32,33/.

4.3 Transportation

Surface transportation is the single largest sector dependent upon petroleum derived fuels. Development of fuel cell powered electric vehicles can make this sector independent of petroleum as electric vehicles can be propelled by fuels derived from nuclear energy or non-exhaustible sources of energy, ie solar energy.

A fuel cell suitable for this application should have short starting time, easy start at subzero temperatures, high energy and power density, high energy efficiency, easy fuel handling, fuel storage and availability of low cost fuel.

Alkaline fuel cells appear ideal for this application. However, it is necessary to lower the cost of electrolytic hydrogen and develop lightweight hydrogen storage containers. The SPE fuel cells also appear suitable for transportation applications but the high capital cost prevents immediate application.

High temperature fuel cells are not suitable since they have very long starting times. Phosphoric acid fuel cells are also unsuitable because of the requirement of an onboard fuel reformer which complicates the power source and reduces the energy density.

Methanol-air cells offer a great advantage of easy methanol handling and distribution. Unfortunately, little effort is being made to develop this fuel cell. If successfully developed SPE based methanol-air fuel cells could easily penetrate the automobile market.

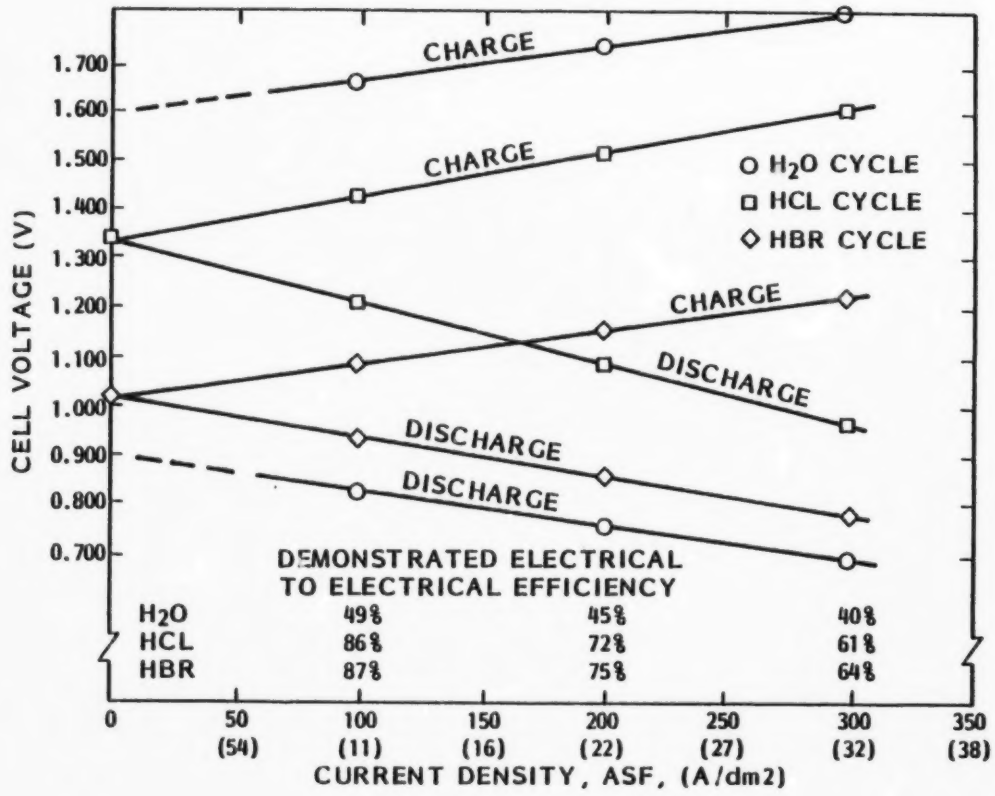

FIGURE 14

DEMONSTRATED AMBIENT TEMPERATURE
SPE REGENERATIVE CYCLES

4.4 Auxiliary Power Sources

Presently lead acid and Ni-Cd batteries are being used as power sources for emergency lighting and turbine starting. Dependability, instantaneous availability of power and high peak power are prerequisites for this application.

SPE and alkaline fuel cells can be used to supplement the power of batteries, where auxiliary power is required for longer periods (more than 15 minutes). Because of the long starting times of all fuel cells, they cannot replace the batteries.

4.5 D_2-O_2 Recombination in Front End Electrolysis Tritium Removal Systems

In the front end electrolysis Tritium Removal Systems, the tritiated moderator water is electrolyzed to obtain a stream of hydrogen isotopes/53/. Tritium is removed from this stream by cryogenic distillation and the detritiated stream of D_2 is recombined with oxygen to yield D_2O/53/. A part of the energy stored in D_2 can be recovered in the form of electrical energy by recombining D_2 with O_2 in a fuel cell.

A fuel cell suitable for this application should have a very low D_2O inventory. Also, minimum steps should be required to free D_2O from the electrolyte. SPE fuel cells appear to be ideal for this application since small deuterium inventories are required in the form of electrolyte and the product is pure D_2O.

5. CONCLUSIONS AND RECOMMENDATIONS

Phosphoric acid and alkaline electrolyte fuel cells are at the most advanced technological stages of development. Of the two, only phosphoric acid cells are flexible enough to run on a variety of reformed carbonaceous fuels and as a result have the potential of being used in power generation. Improvements in the present acid fuel cell technology are needed to lower the cost of cell stacks and improve sintering resistance and carbon monoxide tolerance of the anodes.

Solid polymer electrolyte fuel cell technology is very promising but the high material cost of present cells limits its application to only specialized applications. Other fuel cells under development include molten carbonate and solid oxide fuel cells. Operating at high temperatures (500-1000°C), these technologies offer high energy efficiency and the potential for cogeneration. They are ideally suited for centralized and decentralized generation but numerous material and technological problems remain to be resolved before long-term pilot tests can be started.

It is recommended that work on one or more of the following areas be initiated in order to acquire a better understanding of material and technological developments in fuel cell technologies:

a) Improve life, energy efficiency and fuel flexibility of phosphoric acid fuel cells by:

   i) studying the mechanism of anode sintering. The work can result in new fabrication techniques for anodes with higher sintering resistance.

   ii) developing new, low cost anode and cathode catalysts for phosphoric acid fuel cells, with higher tolerances for CO.

b) Develop low cost oxygen reduction catalysts to improve the performance and lower the capital cost of alkaline fuel cells.

c) Develop the solid polymer electrolyte based methanol-air fuel cells that can ultimately utilize electrolytic hydrogen in the form of methanol.

d) Follow up material and technological developments in molten carbonate and solid oxide fuel cells.

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6. REFERENCES

1. O.T. Melo, "Fuel Cell Power Plant Study", Ontario Hydro Research Division Report No 78-454-K, December 1978.

2. E. Wharton, "Fuel Cell Development", Ontario Hydro Research Division Report No 78-194-H, April 1978.

3. A.G. Barnstaple et al, "Utility Fuel Cell Power Plant Study", Ontario Hydro Report No 79233, July 1979.

4. J. O'M. Bockris and S. Srinivasan, Chapter 3, "Fuel Cells - Their Electrochemistry", McGraw Hill, New York, 1969.

5. J. McBreen, E.J. Taylor, K.V. Kordesh, G. Kissel, F. Kulesa and S. Srinivasan, "Development of Fuel Cell Technology for Vehicular Applications", BNL Report No 51047, August 1979.

6. E.H. Camara, "Status of Phosphoric Acid and Molten Carbonate Fuel Cells", presented at the Winter Meeting of Electrochemical Society, Ontario - Quebec Section, Toronto, February 1982.

7. T. Shirogami, K. Murata, M. Uno and M. Yoshimori, "Performance of the 15 kW Phosphoric Acid Fuel Cell", Abstract No 99, Vol 81-2, Electrochemical Society Inc, Princeton, October 1981.

8. V. Singh, Ontario Hydro Research Division, personal communication, May 1982.

9. F.R. Foulkes, University of Toronto, personal communication, February 1982.

10. J. McBreen et al, "Improved Alkaline Hydrogen/Air Fuel Cells for Transportation Applications", Presented at the 15th Intersoc. Energy Conv. Eng. Conf., August 1980.

11. J. O'M. Bockris and S. Srinivasan, Chapter 10, "Fuel Cells - Their Electrochemistry", McGraw Hill, New York, 1969.

12. J.F. McElroy, "Status of Solid Polymer Electrolyte Fuel Cell Technology", General Electric Co Report, Wilmington, November 1980.

13. B.V. Tilak, R.S. Yeo and S. Srinivasan, "Electrochemical Energy Conversion - Principles", Comprehensive Electrochemistry, Vol III, pl, Ed. J. O'M. Bockris, Plenum Publishing Corp, New York, 1981.

14. H. Broeck, "A Short Review of the Alkaline Fuel Cell Program in Belgium and Netherlands", Progress in Batteries and Solar Cells, Vol 2, Electrochemical Society Press Inc, Cleveland, 1979.

15. K. Kordesch and K. Tomantschger, "Fuel Cells for Electric Vehicles" presented at the Electric Vehicles Exposition, Adelaide, Australia, August 1980.

16. K. Kordesch, "Survey About Carbon and its Role in Phosphoric Acid Fuel Cells", BNL Report No 464459-S, December 1979.

17. K. Mund, G. Richter and F. von Sturm, "Titanium Containing Raney Nickel Catalyst for Hydrogen Electrodes in Alkaline Fuel Cell Systems", J. Electrochemical Society, 124, 1, 1977.

18. K. Huhne, "Air Electrodes for Hydrogen-Air Fuel Cells with Alkaline Electrolyte", Siemens Forsch. Entwicklungsber, 5, 266, 1976.

19. A.M. Trunov, V.A. Presnov, M.V. Uminiskii, O.F. Rakiyanskaya, T.S. Bakutina and A.I. Kotseruba, "Oxygen Reduction at Semi-conductor Catalysts - V. Investigation of Physical and Electrochemical Properties of Mixed Nickel-Cobalt Oxides" Soviet Electrochem. 11, 509, 1975.

20. W.J. King and A.C.C. Tseung, Electrochim Acta, 19, 485, 1974.

21. A.C.C. Tseung and H.L. Bevan, "A Reversible Oxygen Electrode", J. Electroanal Chem, 45, 429, 1973.

22. E.W. Justi and A.W. Karlberlah, Energy Conversion, 8, 47, 1968.

23. A.A. Adams, "Advanced Fuel Cell Electrolyter", Extended Abstract No 103, Vol 81-2, Electrochemical Society, Princeton, N.J., 1981.

24. A.A. Adams and H.J. Barger, Jr., "A New Electrolyte for Hydrocarbon Air Fuel Cells", J. Electrochm Soc, 121, 987, 1974.

25. H. Beheret, H. Binder, W. Clauberg and G. Sandstede, "On the Mechanism of Electrocatalytic Oxygen Reduction With Special Reference to Metal Chelates", Proc Symp on Electrode Materials and Processes for Energy Conversion and Storage, p 519, Vol 77-6, Electrochem Society, Princeton, N.J., 1977.

26. E.J. Cairns and H. Shimotake, "Recent Advances in Fuel Cells and Their Application to New Hybrid Systems", Fuel Cell Systems. American Chemical Society, p.392, 1969.

27. K.R. Williams, M.R. Andrew and F. Jones, "Hydrocarbon Fuel Cell Technology", p. 143, Academic Press, New York, 1965.

28. H. Binder, A. Kohling and G. Sandstede, "Platinum Catalysts Modified by Adsorption or Mixing with Inorganic Substances", 'From Electrocatalysis to Fuel Cells' Univ of Washington Press, Seattle, p 59, 1972.

29. B.D. McNicol, R.T. Short and A.G. Chapman, "Methanol Electro-oxidation Catalysts", J. Chem. Soc., Faraday Trans. 72, 2735, 1976.

30. Internal Document, Urban Transport Development Corporation, September 1981.

31. J.W. Harrison, "Potential of Fuel Cells for Generation of Electricity from Hydrogen", General Electric Co Report, Wilmington, 1980.

32. A.B. LaConti, "Introduction to SPE Cell Technology", General Electric Co Report, Wilmington, 1980.

33. J.F. McElroy, "Status of Solid Polymer Electrolyte Fuel Cell Technology", General Electric Co, Wilmington, 1980.

34. J.R. Selman, T.D. Claar, "Structure and Performance of the Fuel Electrode in the Molten Carbonate Fuel Cell: A Review", Abstract No 374, Vol 82-1, Electrochemical Society Inc, Princeton, N.J., 1982.

35. M.W. Breiter,'Electrochemical Processes in Fuel Cells' Springer - Verlag New York Inc, 1969.

36. K.R. Williams, 'An Introduction to Fuel Cells", Elsevier Publishing Co, New York, 1966.

37. A. Gelb and G. Wilemski, "Structure and Performance of the Fuel Cell Electrode in the Molten Carbonate Fuel Cell: A Review", Abstract No 373, Vol 82-1, Electrochemical Society Inc, Princeton, N.J., 1982.

38. E.T. Ong and T.D. Claar, "Electrolyte Vapourization Losses from Molten Carbonate Fuel Cells", Abstract No 372, Vol 82-1, Electrochemical Society Inc, Princeton, 1982.

39. B.S. Baker, "Molten Carbonate Fuel Cell Technology - The Past Decade", Abstract No 369, Vol 82-1, Electrochemical Society Inc, Princeton, N.J., 1982.

40. D.L. Johnston and N.M. Sbrockey, "Inhibition of Sintering of Molten Carbonate Fuel Cell Anode Materials", Abstract No 376, Vol 82-1, Electrochemical Society Inc., Princeton, N.J., 1982.

41. R.D. Pierce, R.M. Adams and J.L. Smith, "Cathode Development for Molten Carbonate Fuel Cells", Abstract No 378, Electro-chemical Society Inc, Princeton, N.J., 1982.

42. C.E. Baumgartner, "Molten Carbonate Fuel Cell Cathode Studies", Abstract No 379, Vol 82-1, Electrochemical Society Inc, Princeton, N.J., 1982.

43. D.T. Hooie, "Critical Issues in Advanced Fuel Cell Technology", Abstract No 390, Vol 82-1, Electrochemical Society, Inc, Princeton, N.J., 1982.

44. R.E. Carter, W.E. Rocco, H.S. Spacil and W.E. Tragert, General Electric Press Release, December 1962.

45. F.J. Rohr, "High Temperature Solid Oxide Fuel Cells: Present State and Problems of Development", Proc Workshop on High Temperature Solid Oxide Fuel Cells, p 122, 1977.

46. T.H. Etsell, "Summary of Panel Session on Electrodes", Proc Workshop on High Temperature Solid Oxide Fuel Cells, p 60, 1977.

47. M. Warshay, "Discussion of Potential of High Temperature Solid Oxide Fuel Cell Power Plant Systems", Proc Workshop on High Temperature Solid Oxide Fuel Cells, p 90, 1977.

48. G.P. Wirtz, "Summary of Panel Discussion on Interconnection Materials", Proc Workshop on High Temperature Solid Oxide Fuel Cells, p 30, 1977.

49. T.H. Etsell, "Performance of Solid Oxide Fuel Cell Electrodes", Proc Workshop on High Temperature Solid Oxide Fuel Cells, p 66, 1977.

50. P.G. Russel, H.S. Isaacs, A.C.C. Tseung, "Studies on Glass Composition and Doped Rutile as Interconnection Materials", Proc Workshop on High Temperature Solid Oxide Fuel Cells, p 96, 1977.

51. P. Steitz and D. Dotson, "Identifying Prospective Users of Fuel Cell Power Plants", EPRI Report No EM2480, June 1982.

52. A.G. Barnstaple, Ontario Hydro Design and Development Division, personal communication, November 1981.

53. A.G. Barnstaple, Ontario Hydro Design and Development Division, in letter addressed to I.D. Carnegie, Pratt and Whitney Aircraft of Canada Ltd, Longueil, May 1981.